

PATENT SPECIFICATION

NO DRAWINGS

1,162,702



Date of Application (No. 40046/66) and filing Complete Specification: 7 Sept., 1966.

Application made in United States of America (No. 487,315) on 14 Sept., 1965.

Complete Specification Published: 27 August, 1969.

Index at acceptance:—C7 D(8K, 8M, 8Q, 8R, 9B1A, 9B2B, 9B3D, A1); C7 A(A249, A279, A28Y, A28X, A30Y, A313, A316, A319, A339, A349, A35Y, A362, A364, A389, A409, A439, A459, A509, A529, A549, A55Y, A562, A565, A568, A57Y, A599, A609, A629, A67X, A671, A673, A675, A677, A679, A68X, A681, A683, A685, A687, A689, A69X, A693, A695, A697, A699, A70X, 71X, 747, 78Y)

International Classification:—B 22 f 1/00

COMPLETE SPECIFICATION

Low Alloy Iron Powder and process of preparing the same

We, HOGANAS-BILLESHOLMS AKTIEBOLAG, a Swedish joint stock company, of Hoganas, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to powder metallurgy and relates more particularly to an improved process of preparing a low alloy iron powder having a low dimensional change when heat treated after being formed into articles as well as a high level of strength.

10 The use of iron base powders to form powder metallurgy parts is well-known in the art. In addition, it is also well known to add alloying elements such as carbon, molybdenum, manganese, phosphorus and nickel, to improve the mechanical properties under three conditions: (1) in the pressed and sintered condition; (2) in the pressed, sintered and re-pressed condition; and (3) in the pressed, sintered, repressed and resintered condition. The addition of alloying elements also renders the material more easily heat treatable. There are many combinations in use which involve the mixing of the alloying elements in the form of elemental powder so that the alloys will be formed by diffusion during the sintering and

15 heat treating processes. In general, the addition of alloying elements in powder form increases the strength of the finished articles but certainly not to the extent that one would normally expect when a comparison is made with wrought materials. Also, it has been sometimes necessary to heat treat the alloy powders of the prior art at high temperatures for a long time in carefully controlled sintering atmospheres, thereby detracting from one of the

more important aspects of producing parts by the powder metallurgy method, namely, low cost.

40 Another limitation of most of the prior methods of producing alloyed articles by powder metallurgy processes is the lack of dimensional stability during the sintering and heat treating processing. The high temperatures cause considerable dimensional shrinkage, sometimes as much as three percent. This fact reduces another important advantage which is generally regarded as advantageous for the powder metallurgy process, namely, the ability to produce parts to close dimensional tolerance without machining or other secondary operations.

45 50 55 60 65 70 75

Another limitation of most of the prior methods of producing alloyed articles by powder metallurgy processes is the lack of dimensional stability during the sintering and heat treating processing. The high temperatures cause considerable dimensional shrinkage, sometimes as much as three percent. This fact reduces another important advantage which is generally regarded as advantageous for the powder metallurgy process, namely, the ability to produce parts to close dimensional tolerance without machining or other secondary operations.

Alloy-type powders have been made by first producing the alloy by the molten process and then converting this material into powder by atomization. Such a powder is not completely satisfactory because it is quite hard, difficult to press into a desired shape, and the strength of the pressed article is quite low. Even after sintering, the strength of the final article is considerably less than desired unless extreme conditions of time and temperature are employed.

The present invention was developed to try to overcome the shortcomings reviewed above.

The present invention provides a process for preparing a low alloy powder suitable for use in powder metallurgy comprising heating an unalloyed mixture of iron powder, a molybdenum compound, copper or a copper compound, a nickel or a nickel compound in a reducing atmosphere at a temperature below the melting point of the mixture but sufficiently high to cause prealloying of the mixture and agglomeration of the particles thereof, dis-

[Price 4s. 6d.]

continuing the heating before complete alloying of the mixture occurs, and then grinding the agglomerated particles. The purpose of the prealloy anneal step of the process of the present invention is to create a powder in which the alloy content is partially alloyed, enough to ensure adequate diffusion during sintering, but not enough to substantially increase the hardness of the particles and thus increase the pressure required to press the powder. The prealloy treatment produces "active" alloy ingredients which start to diffuse into the base iron. This alloying is limited in degree by the time and temperature of annealing. This is desired in order to preserve the good compressibility of the base iron. When the resulting powder is pressed into parts and the sintered at temperatures above about 2000°F., the alloying elements further diffuse, the extent of diffusion being greater than if the powders had not been subjected to this prealloy anneal. The resulting metallurgical structure is more uniform and is more easily heat treated. The prealloy anneal is preferably conducted at a temperature not higher than 1850°F. Satisfactory prealloy is usually accomplished in the temperature range of 1,300°F. to 1,850°F. for a time interval within the range of 15 to 60 minutes. At the low temperature ranges a longer time is required for a sufficient degree of prealloying. On the other hand, annealing for 30 minutes at 1,850°F produces enough alloying to cause the compressibility of the powder to substantially decrease. For example, for powder produced by annealing at 1,350°F. and 1,600°F. a briquetting pressure of only 33 tons per square inch is required to obtain a density of 6.5 grams per cubic centimeter, while powder annealed at 1,850°F. requires 41 tons per square inch to obtain the same density. The prealloy anneal step of the process of this invention, particularly at the higher end of the preferred temperature range, causes considerable bonding of particles even when relatively coarse iron is used. For this reason, the powder has to be ground afterwards. This grinding tends to work-harden the particles and in order to restore their softness and thereby improve the compressibility it is desirable to subject the powder to a softening anneal at a temperature below that at which there is substantial agglomeration of the particles, and preferably at about 1350°F. for about 30 minutes. As little agglomeration takes place, normal handling or screening is sufficient to break the product down to the desired size of 177 microns or less. The alloying ingredients should be dispersed as uniformly as possible in the base iron. One method of obtaining a fine, uniform distribution of alloying elements is to use water soluble salts of nickel, molybdenum and copper dissolve in water which is then mixed with the iron powder. Preferably, sufficient water to completely wet the iron powder is used to ensure complete coverage. Among the soluble compounds which may be used are nickel nitrate, nickel formate, nickel glyoxime, ammonium molybdate, molybdenum nitrate, copper formate and copper nitrate. After drying, the salts may react chemically with the iron or may precipitate in their original composition on the surface of the iron. During annealing the salts decompose or are reduced to the metal state and then start to diffuse into the iron. Another method of obtaining uniform dispersion of the alloying ingredients in the mixture is to use fine powders, e.g. of particle sizes less than 200 microns, which are mixed by any of the many commercial methods of mixing (either dry or wet), such as tumbling, ball mixing and milling. For this method, elemental nickel in the form of very fine powder (less than 5 microns), such as produced by the carbonyl process, is preferably used, although reducible compounds of nickel such as nickel oxide, nickel carbonate and nickel stearate can also be employed. On the other hand it is preferred to use a compound of copper rather than this metal in elemental form. The preferred copper compound is copper oxide since the use of this material results in substantially less increase in sintering size than when copper powder is used. Thus, by using copper oxide, enough copper can be added for increased strength without causing excessive sintered growth. Suitable molybdenum compounds which can be used in this invention are molybdenum trioxide, molybdic acid and ammonium molybdate, the first-mentioned compound being preferred since during the initial stages of heating, the reducing action of the reducing gas employed is insufficient to reduce the trioxide so that this material first vaporizes at about 1000°F. and in this form spreads evenly throughout the mass of the powder, to be subsequently reduced to nascent molybdenum which condenses as extremely fine elemental molybdenum throughout the powder. The base iron can be iron powder in any form, but preferably one made by reduction of iron ore which has a high specific surface which allows for better alloy distribution. The particle size of the iron powder can range from 70 microns down to sub-micron size, but the average particle size is from 5 to 20 microns. When the average particle size is below 20 microns, it is preferred to carry out the prealloy anneal at the higher end of the preferred temperature range of 1350° — 1850°F in order to agglomerate the particles sufficiently to increase the average particle size to 20 — 40 microns, thereby largely eliminating the fines which cause sticking difficulties when the powder is pressed between a punch and a die. When molybdenum trioxide is used to provide the molybdenum component, a small amount

70

75

80

85

90

95

100

105

110

115

120

125

130

of unreduced iron oxide (about 0.40 to 0.50 weight percent) should be present in the base powder to provide oxygen for the purpose of preventing instantaneous reduction of the molybdenum trioxide.

Small quantities of a binder such as polyvinyl alcohol, gum or starch, may also be added to the mixture to reduce the loss of material through dusting. Also, carbon-containing additives such as graphite and stearic acid in amounts of about 0.5% by weight of the mixture may be added to promote reduction during the prealloy annealing.

After the mixture of base iron and alloying

ingredients has been prepared, and if necessary dried, as by conventional means, the mixture is subjected to the prealloy anneal heating in an atmosphere of a reducing gas. Suitable reducing gases are dissociated ammonia and hydrogen. After annealing, the powder is ground to a desired size which may be 40 mesh (U.S. standard) or smaller and then preferably annealed at approximately 1,350°F. to relieve the stresses introduced by grinding. The powder is now ready for use for powder metallurgical purposes. A typical powder obtained by the process of the present invention has the following characteristics:

| | |
|------------------|---|
| Flow | 33 sec. ASTM Spec. |
| Apparent Density | 2.3 to 2.6 grams per inch |
| Green Strength | 2,000 pounds per square inch |
| Fines Content | 20% — 352 mesh |
| Compressibility | 6.2 grams per cc at 30 tons per square inch |

In order to achieve best results, it is desirable to limit the weight composition of the powders produced by this invention to the following ranges:

| | | |
|------------|--------------|------------------------|
| Nickel | 1.50 — 3.00% | 1.7 — 2% preferred |
| Molybdenum | 0.40 — 1.00% | 0.40 — 0.60% preferred |
| Copper | 0.50 — 2.0% | 1.40 — 1.60% „ |
| Iron | Balance | |

Each of the ingredients is easily protected from oxidation during sintering by a protective atmosphere such as dissociated ammonia, purified exothermic gas and endothermic gas.

The selection of the alloying elements is to some extent based on considerations which are well known in the metallurgical field. Thus, the molybdenum is added to increase the basic strength of the iron and to increase its ability to be hardened. The nickel is a mild base iron strengthener and also aids hardening ability. In addition, it imparts toughness. Copper is normally added to solid iron for slight increases in strength, but mainly for increased corrosion resistance.

The selection of the alloying elements and of their relative proportions in the powder of this invention is, however, also to a great ex-

tent based on their influence on size change during sintering and during heat treatment. This is, in fact, the most important consideration. The nickel causes excessive shrinkage which is only partially compensated for by the molybdenum. Enough copper is added to reduce the shrinkage to a minimum. In other words, the final composition is chosen so that after sintering and heat treatment, the parts made from this powder vary very little from the dimensions of the briquetting die. Thus, no allowances need be made for size change and, in addition, the dies used for briquetting can also be used for repressing or sizing.

The following Table compares various physical and mechanical properties of powder made according to this invention and those of similar powders made by other methods.

15

20

25

55

60

65

70

TABLE
(Density 6.5 g/cc)

| | Briq. Pres. | Transverse Rupture Strength | Hardness | Size Change, % |
|--------------------------|----------------|-----------------------------------|----------|----------------------|
| Atomized Prealloy I | | | | |
| As Sintered | 30 TSI | 98,500 | Rb 72 | -.04 |
| As Heat Treated | | 115,300 | Ra 73 | -.04 |
| Atomized Prealloy II | | | | |
| As Sintered | 40 TSI | 121,800 | Rb 76 | -.16 |
| As Heat Treated | | 124,800 | Ra 68 | -.18 |
| Atomized Prealloy III | | | | |
| As Sintered | 48 TSI | 112,600 | Rb 78 | -.1.10 |
| As Heat Treated | | 129,800 | Ra 70 | -.1.04 |
| 114,000 | | | | |
| Admixed Elemental Powder | | | | |
| As Sintered | 33.5 TSI | 121,100 | Rb 79 | +.23 |
| As Heat Treated | | 139,100 | Ra 67 | -.18 |
| Present Invention | | | | |
| As Sintered | 33.5 TSI | 122,300 | Rb 74 | -.06 |
| As Heat Treated | | 200,000 | Ra 66 | -.10 |

The data shown in the foregoing table illustrates the fact that the powder produced in accordance with the present invention possesses the following desirable attributes:

5 1. Good compressibility.
2. High mechanical properties in the pressed and sintered conditions and particularly good properties in the pressed, sintered and heat treated condition.
10 3. Very low dimensional change during sintering and during heat treatment.

WHAT WE CLAIM IS:—

15 1. A process for preparing a low alloy powder suitable for use in powder metallurgy, comprising heating an unalloyed mixture of iron powder, a molybdenum compound, copper or a copper compound, and a nickel or a nickel compound in a reducing atmosphere at a temperature below the melting point of the mixture but sufficiently high to cause prealloying of the mixture and agglomeration of the particles thereof, discontinuing the heating before complete alloying of the mixture occurs, and then grinding the agglomerated particles.
20 2. A process according to Claim 1, wherein said mixture is heated at a temperature of from 1300°F to 1850°F for from 60 minutes to 15 minutes.
25 3. A process according to Claim 1 or Claim 2, wherein the ground particles are annealed to relieve the stresses produced by grinding

at a temperature below that at which there is substantial agglomeration of the particles.

35

4. A process according to any preceding claim, wherein hydrogen or dissociated ammonia provides the reducing atmosphere.

40

5. A process according to any preceding claim, wherein said mixture is prepared by mixing the iron powder with the alloying ingredients in powder form.

45

6. A process according to Claim 5, wherein elemental nickel is used.

45

7. A process according to Claim 5 or Claim 6, wherein molybdenum trioxide is used.

50

8. A process according to any one of Claims 5—7, wherein a copper oxide is used.

50

9. A process according to any one of Claims 1—4, wherein said mixture is prepared by mixing the iron powder with an aqueous solution containing dissolved salts of the alloying ingredients, and thereafter drying the iron powder.

55

10. A process according to any preceding claim, wherein said mixture contains also a binder selected from polyvinyl alcohol, gums and starch.

60

11. A process for preparing a low alloy powder suitable for use in powder metallurgy, according to Claim 1 and substantially as hereinbefore described.

65

12. A low alloy powder suitable for use in powder metallurgy, whenever prepared by a process according to any preceding claim.

13. A powder according to Claim 12, comprising 0.4—1.0% by weight molybdenum, and 0.5—2.0% by weight copper.

14. A powder according to Claim 13, comprising 1.7—2.0% by weight nickel, 0.4—0.6% by weight molybdenum, and 1.4—1.6% by weight copper.

15. A sintered article formed from a powder according to any one of Claims 12—14.

TREGEAR, THIEMANN, & BLEACH,
Chartered Patent Agents,
Melbourne House, Aldwych,
London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.

13. A powder according to Claim 12, comprising 0.4—1.0% by weight molybdenum, and 0.5—2.0% by weight copper.

14. A powder according to Claim 13, comprising 1.7—2.0% by weight nickel, 0.4—0.6% by weight molybdenum, and 1.4—1.6% by weight copper.

15. A sintered article formed from a powder according to any one of Claims 12—14.

TREGEAR, THIEMANN, & BLEACH,
Chartered Patent Agents,
Melbourne House, Aldwych,
London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.

THIS PAGE BLANK (USPTO)